

The structure of fluids with impurities

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The influence of dilute impurities on the structure of a fluid solvent is investigated theoretically. General arguments, which do not rely on particular models, are used to derive an extension of the Ornstein-Zernike form for the solvent structure factor at small scattering vectors. It is shown that dilute impurities can influence the solvent structure only if they are composed of ions with significantly different sizes. Non-ionic impurities or ions of similar size are shown to not alter the solvent structure qualitatively. This picture is compatible with available experimental data. The derived form of the solvent structure factor is expected to be useful to infer information on the impurity-solvent interactions from measured scattering intensities.

Dedicated to Matthias Ballauff on the occasion of his 60th birthday.

I. INTRODUCTION

Scattering techniques are powerful approaches to infer structural properties of soft materials. In various combined experimental and theoretical studies, Matthias Ballauff has contributed much insight into this topic by successfully comparing partial structure factors calculated from Ornstein-Zernike equations with experimentally determined scattering data of dissolved dendrimers¹⁻⁴, bottle-brush polymers^{5,6}, polyelectrolyte brushes^{7,8}, plate-like colloids⁹, and nanoparticles^{10,11}. In these earlier studies the Ornstein-Zernike equations have been employed in the study of pair correlations of the dissolved particles. However, due to complex preparation procedures, many fluids contain impurities, which potentially influence the solvent structure factor even in the case of highly diluted impurities¹²⁻¹⁵. In the following we address the problem of how impurities can alter the form of the solvent structure factor. By means of general, model independent arguments based on Ornstein-Zernike equations we derive a general asymptotic form of the solvent structure factor. This form of the solvent structure factor and the insight gained from it is expected to be useful also for the analysis of future studies involving impurities in fluid systems.

In the next Sec. II the setting is defined and a detailed mathematical derivation of the asymptotic structure factor is given. The consequences of this asymptotic form are discussed in Sec. III. Finally, conclusions and a summary are given in Sec. IV.

II. MATHEMATICAL PART

A. Setting

Consider a spatially uniform fluid mixture of three components of which component 1 is referred to as the

“solvent” whereas components 2 and 3 are called “impurities”. The interaction potentials $U_{ij}(r)$ between two particles of components i and j are assumed to be isotropic and vanishing at infinite particle separation ($r \rightarrow \infty$). Note that no particular asymptotic decay of $U_{ij}(r \rightarrow \infty)$ is assumed. The mole fraction x_i of component $i \in \{1, 2, 3\}$ may be expressed in terms of the mole fraction $x = x_2 + x_3$ of impurities and the composition $\phi \in [0, 1]$ of the impurities such that $x_1 = 1 - x$, $x_2 = \phi x$ and $x_3 = (1 - \phi)x$. For *ionic* impurities with valencies $z_2, z_3 > 0$ of the respective components the constraint $z_2 x_2 = z_3 x_3$ of local charge neutrality of the bulk fluid leads to the composition $\phi = z_3/(z_2 + z_3)$, whereas the composition ϕ of *non-ionic* impurities is not restricted to a particular value.

B. Solvent structure factor

In general the partial structure factors $S_{ij}(q)$ with $i, j \in \{1, 2, 3\}$ of a fluid with total number density ϱ are given by¹⁶

$$S_{ij}(q) = \sqrt{x_i x_j} \delta_{ij} + x_i x_j \varrho \hat{h}_{ij}(q), \quad (1)$$

where

$$\hat{h}_{ij}(q) = \frac{4\pi}{q} \int_0^\infty r h_{ij}(r) \sin(qr) \quad (2)$$

is the (three-dimensional) Fourier transform of the total correlation function $h_{ij}(r) = g_{ij}(r) - 1$. Here q denotes the magnitude of the scattering vector and $g_{ij}(r)$ is the radial distribution function. As the name implies, the total correlation function $h_{ij}(r)$ gives a complete information about all the correlations between a pair of particles of components i and j . By considering $S_{ij}(q)$ and $\hat{h}_{ij}(q)$ as the (i, j) -components of the matrices $\underline{S}(q)$ and $\hat{\underline{h}}(q)$, respectively, and with the diagonal matrix $\underline{x} := \text{diag}(x_1, x_2, x_3)$ one can rewrite Eq. (1) in the matrix form

$$\underline{S}(q) = \sqrt{\underline{x}} (\underline{1} + \varrho \sqrt{\underline{x}} \hat{\underline{h}}(q) \sqrt{\underline{x}}) \sqrt{\underline{x}}. \quad (3)$$

The Ornstein-Zernike equation links $\hat{h}_{ij}(q)$ to the Fourier transform $\hat{c}_{ij}(q)$ of the direct correlation function $c_{ij}(r)$ ¹⁶:

$$\hat{h}_{ij}(q) = \hat{c}_{ij}(q) + \varrho \sum_k x_k \hat{c}_{ik}(q) \hat{h}_{kj}(q) \quad (4)$$

or in an equivalent matrix form

$$(\mathbf{1} + \varrho \sqrt{\mathbf{x}} \hat{\mathbf{h}}(q) \sqrt{\mathbf{x}}) (\mathbf{1} - \varrho \sqrt{\mathbf{x}} \hat{\mathbf{c}}(q) \sqrt{\mathbf{x}}) = \mathbf{1}. \quad (5)$$

Hence the matrix of partial structure factors $\underline{S}(q)$ is given by

$$\underline{S}(q) = \sqrt{\mathbf{x}} (\mathbf{1} - \varrho \sqrt{\mathbf{x}} \hat{\mathbf{c}}(q) \sqrt{\mathbf{x}})^{-1} \sqrt{\mathbf{x}}. \quad (6)$$

Introducing $\gamma_{ij} := \varrho \sqrt{x_i x_j} \hat{c}_{ij}(q)$ for given q one obtains from Eq. (6) by means of Cramer's rule the solvent partial structure factor

$$S_{11}(q) = \frac{x_1}{1 - \gamma_{11} - \frac{\gamma_{12}^2(1 - \gamma_{33}) + \gamma_{13}^2(1 - \gamma_{22}) + 2\gamma_{12}\gamma_{13}\gamma_{23}}{(1 - \gamma_{22})(1 - \gamma_{33}) - \gamma_{23}^2}} \quad (7)$$

C. Direct correlation functions

Since the Ornstein-Zernike equation is a definition of the direct correlation function $c_{ij}(r)$, it does not yield a method of calculating this correlation function. In order to proceed, the asymptotic behaviour $\hat{c}_{ij}(q \rightarrow 0)$ of the Fourier transform of the direct correlation function $c_{ij}(r)$ is required. It is known¹⁶ that $c_{ij}(r > R_{ij}) \simeq -\beta U_{ij}(r)$ with $1/\beta = k_B T$ for sufficiently large $R_{ij} > 0$. Hence $\hat{c}_{ij}(q) = \hat{c}_{ij}^<(q) + \hat{c}_{ij}^>(q)$ with

$$\hat{c}_{ij}^<(q) = \frac{4\pi}{q} \int_0^{R_{ij}} r c_{ij}(r) \sin(qr) \quad (8)$$

being an even entire function of q and

$$\hat{c}_{ij}^>(q) = -\frac{4\pi}{q} \int_{R_{ij}}^{\infty} r \beta U_{ij}(r) \sin(qr). \quad (9)$$

If $\beta U_{ij}(r) = A_{ij}/r$ one obtains

$$\hat{c}_{ij}^>(q) \simeq -\frac{4\pi A_{ij}}{q^2} + f_{ij}^>(q) \quad (10)$$

with an even entire function $f_{ij}^>(q)$ of q . However, if $\beta U_{ij}(r)$ decays faster than $\mathcal{O}(1/r)$, including power laws $\propto 1/r^n$, $n \geq 2$, and all short-ranged interaction potentials, $\hat{c}_{ij}^>(q)$ is an even entire function of q . Hence the Fourier transform $\hat{c}_{ij}(q)$ is of the general form

$$\hat{c}_{ij}(q) \simeq -\frac{4\pi A_{ij}}{q^2} + f_{ij}(q) \quad (11)$$

with an even entire function $f_{ij}(q)$ of q and with a coefficient A_{ij} , which vanishes if $\beta U_{ij}(r \rightarrow \infty)$ decays faster than $\mathcal{O}(1/r)$.

D. Asymptotic solvent structure factor

For small mole fraction $x \ll 1$ of impurities and inverse scattering vector magnitudes $1/q$ larger than the particle sizes, the general form Eq. (11) of the Fourier transform $\hat{c}_{ij}(q)$ of the direct correlation function $c_{ij}(r)$ leads to the following expressions of γ_{ij} defined in Subsec. II B:

$$\gamma_{11} \simeq \varrho(c_{11}^{(0)} + c_{11}^{(1)} q^2) \quad (12)$$

$$\gamma_{12} \simeq \varrho \sqrt{x\phi} (c_{12}^{(0)} + c_{12}^{(1)} q^2) \quad (13)$$

$$\gamma_{13} \simeq \varrho \sqrt{x(1-\phi)} (c_{13}^{(0)} + c_{13}^{(1)} q^2) \quad (14)$$

$$\gamma_{22} \simeq \varrho x \phi \left(-\frac{4\pi \ell_B z_2^2}{q^2} + c_{22}^{(0)} + c_{22}^{(1)} q^2 \right) \quad (15)$$

$$\gamma_{33} \simeq \varrho x (1-\phi) \left(-\frac{4\pi \ell_B z_3^2}{q^2} + c_{33}^{(0)} + c_{33}^{(1)} q^2 \right) \quad (16)$$

$$\gamma_{23} \simeq \varrho x \sqrt{\phi(1-\phi)} \left(\frac{4\pi \ell_B z_2 z_3}{q^2} + c_{23}^{(0)} + c_{23}^{(1)} q^2 \right), \quad (17)$$

where $c_{ij}^{(0)}$ and $c_{ij}^{(1)}$ are the expansion coefficients of the entire parts $f_{ij}(q)$ of $\hat{c}_{ij}(q)$ (see Eq. (11)) in $q = 0$ and $A_{22} = \ell_B z_2^2$, $A_{33} = \ell_B z_3^2$, $A_{23} = -\ell_B z_2 z_3$, where ℓ_B denotes the Bjerrum length. In the case of non-ionic impurities, i.e., $z_2 = z_3 = 0$, no pole occurs at $q = 0$ in Eqs. (15)–(17).

In the absence of impurities, i.e., for $x = 0$, one obtains the well-known Ornstein-Zernike structure factor $S_{11}(q) = (1 - \varrho(c_{11}^{(0)} + c_{11}^{(1)} q^2))^{-1}$ from Eqs. (7) and (12). From the relation $S_{11}(0) > 0$, which holds due to the fact that $S_{11}(0)$ is the ratio between the compressibility of the solvent and that of a gas of non-interacting particles of the same temperature and density¹⁶, one infers $1 - \varrho c_{11}^{(0)} \geq 0$. Moreover, $c_{11}^{(1)} < 0$ is required if the bulk phase diagram of the pure solvent exhibits critical points and if the pure solvent is uniform throughout the whole one-phase region of the bulk phase diagram, i.e., $S_{11}(q)$ for $q > 0$ does not diverge even close to critical points. Note that these conditions are not fulfilled by a fluid of hard spheres, because there is no critical point in the corresponding bulk phase diagram, which is independent of temperature and exhibits only a first-order phase transition.

Inserting Eqs. (12)–(17) into Eq. (7) and considering only the dominant contributions in the mole fraction $x \ll 1$ of impurities leads to the asymptotic form

$$S_{11}(q) \simeq \frac{S_{11}(0)}{1 + (\xi q)^2 \left(1 - \frac{g^2}{1 + (q/\kappa)^2} \right)}, \quad (18)$$

where

$$S_{11}(0) = \frac{1}{1 - \varrho(1-x)c_{11}^{(0)} - \varrho^2 x (\phi c_{12}^{(0)} + (1-\phi)c_{13}^{(0)})^2} \quad (19)$$

is related to the compressibility of the solvent¹⁶, $\xi = \sqrt{-\varrho c_{11}^{(1)} S_{11}(0)}$ is the bulk correlation length and $\kappa =$

$\sqrt{8\pi\ell_B I}$ is the inverse Debye length with $I = \varrho x(z_2^2\phi + z_3^2(1-\phi))/2$ denoting the ionic strength. The quantity

$$g^2 := \frac{(c_{12}^{(0)} - c_{13}^{(0)})^2}{-4\pi\ell_B c_{11}^{(1)}(z_2 + z_3)^2} \quad (20)$$

measures the contrast of impurity-solvent interactions. Hence the normalized solvent structure factor $S_{11}(q)/S_{11}(0)$ depends on the two dimensionless parameters $\kappa\xi$ and g^2 which are related to material parameters such as $\varrho, x, \phi, z_2, z_3$, and ℓ_B . The form of Eq. (18) has previously been derived in Ref.¹⁷ within a specific model of electrolyte solutions. The derivation presented here demonstrates that the asymptotic form Eq. (18) of the solvent structure factor $S_{11}(q)$ is independent of any specific model. The consequences of Eqs. (18)–(20) and the physical meaning of the quantity g^2 are discussed in the following section.

III. DISCUSSION

A. Forms of the solvent structure factor

Considering $S_{11}(q)$ in Eq. (18) one immediately recognizes

$$S_{11}(q) \simeq \begin{cases} \frac{S_{11}(0)}{1 - g^2(\kappa\xi)^2 + (\xi q)^2} & , q \gg \kappa \\ \frac{S_{11}(0)}{1 + (1 - g^2)(\xi q)^2} & , q \ll \kappa. \end{cases} \quad (21)$$

In particular, for non-ionic impurities, i.e., for $\kappa = 0$, the solvent structure factor $S_{11}(q) \simeq S_{11}(0)/(1 + (\xi q)^2)$ is not altered to leading order in the mole fraction x . However, ionic impurities due to, e.g., alkali halides of ionic strength $I \approx 1$ mM in water at room temperature, i.e., $x \approx 4 \cdot 10^{-5}$, lead to a Debye length $1/\kappa \approx 10$ nm which is much larger than the particle size.

For ionic impurities it is readily seen that $S_{11}(q)$ is monotonically decreasing with q if $|g| \leq 1$ (see Figs. 1(a) and (b)). If $|g| > 1$ a maximum of $S_{11}(q)$ occurs at $q = q_{\max} = \kappa\sqrt{|g| - 1}$. In this latter case $S_{11}(q_{\max}) = S_{11}(0)/(1 - (\kappa\xi(|g| - 1))^2)$ is finite for $\xi < (\kappa(|g| - 1))^{-1}$ (see Fig. 1(c)), whereas $S_{11}(q)$ has a pole for $\xi \geq (\kappa(|g| - 1))^{-1}$ (see Fig. 1(d)). Obviously, whenever $|g| > 1$, a divergence of $S_{11}(q)$ occurs upon approaching a critical point, where the bulk correlation length ξ diverges. Hence, by adding ionic impurities the solvent remains uniform within the whole one-phase region of the bulk phase diagram if and only if $|g| \leq 1$, i.e., if the contrast of impurity-solvent interactions is sufficiently small. This can be understood in such a way that a contrast of impurity-solvent interactions ($|g| > 0$) promotes density fluctuations of a particular finite wave length $2\pi/q_{\max}$ which occur upon approaching a critical point. The question on the origin of a sufficiently strong contrast of impurity-solvent interactions is addressed in the following Subsec. III B.

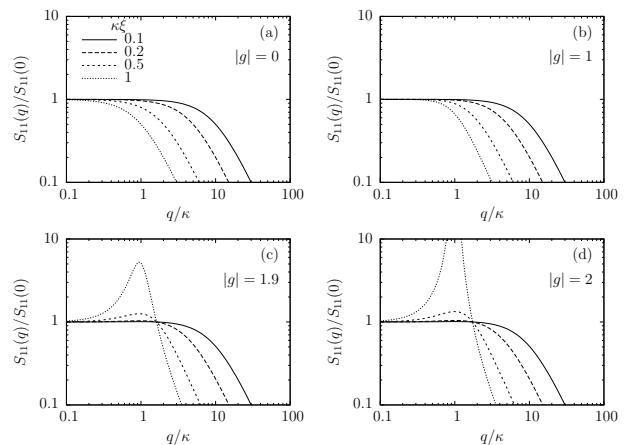


FIG. 1. Influence of dilute ionic impurities on the solvent structure factor $S_{11}(q)$. The bulk correlation length is denoted by ξ , whereas the inverse Debye length is given by κ . The contrast of impurity-solvent interactions is measured by the parameter $|g|$ (see Eq. (20)). For $|g| \leq 1$ (panels (a) and (b)) a monotonic structure factor is found, whereas a non-monotonic behaviour with a maximum close to the Debye length $1/\kappa$ occurs for $|g| > 1$ (panels (c) and (d)). In the latter situation the maximum diverges at a sufficiently large but finite bulk correlation length (panel (d)).

B. Contrast of impurity-solvent interactions

It has been shown in the previous Subsec. III A that deviations from a monotonic Ornstein-Zernike-like solvent structure factor $S_{11}(q)$ occur only for *ionic* impurities *and* for a sufficiently *large contrast* of impurity-solvent interactions ($|g| > 1$). Non-monotonic solvent structure factors have indeed been found in heavy water+3-methylpyridine mixtures in the presence of sodium tetraphenylborate (NaBPh_4) by means of small-angle neutron scattering¹⁴. However, the same solvent under the same conditions with simple salt impurities (LiCl , NaCl , NaBr , KCl and MgSO_4) led to monotonic solvent structure factors^{12,13}. This experimental observation implies that the valency of impurity ions are *not* expected to be the origin for impurity-induced non-uniformities of the solvent. In agreement with this, it has recently been concluded within a theoretical model¹⁸ that neither the valency nor differences in solubility give rise to a sufficiently large parameter $|g| > 1$.

Here it is proposed that $|g| > 1$ may be reached due to steric effects, i.e., due to the property of (ionic) impurities being structure-makers or structure-breakers. For spherical particles $c_{12}^{(0)} \propto (R_1 + R_2)^3$ and $c_{13}^{(0)} \propto (R_1 + R_3)^3$ can be expected, where R_i denotes the extension of a particle of component i . Hence, according to Eq. (20), $|g| > 1$ may be reached for impurities of significantly different particle sizes such as Na^+ and $[\text{BPh}_4]^-$, whereas $|g| < 1$ for particles of similar size like simple salts. Non-monotonic solvent structure factors can be measured using small-angle neutron or x-ray scattering in

view of the aforementioned typical Debye length $1/\kappa$ and $q_{\max}/\kappa = \sqrt{|g| - 1}$. In the case of highly diluted impurities the functional shape of the measured scattering intensity is dominated by the solvent structure factor.

It is important to understand that it is not the valency but the long-ranged character ($\propto 1/r$) of electrostatic interactions of the impurities which gives rise to the relevance of the parameter $|g|$ for the formation of a non-uniform solvent structure. However, whether the solvent becomes non-uniform upon adding ionic impurities is mainly determined by the size-differences between the impurity particles.

IV. CONCLUSIONS AND SUMMARY

By means of general, model independent properties of the direct correlation functions it has been shown that dilute impurities may influence the structure of a solvent if and only if they are composed of ions with a sufficiently

large contrast of impurity-solvent interactions. It has been argued that the latter feature requires significantly different particle sizes. Non-ionic impurities or ions of similar size are not expected to give rise to a qualitative change in the large-scale structure of the solvent. Ionic impurities with a sufficiently strong impurity-solvent interaction contrast lead to a non-monotonic solvent structure factor with a maximum at a magnitude of the scattering vector close to the inverse Debye length (Fig. 1). Upon approaching a critical point, this maximum height diverges at a finite bulk correlation length, which corresponds to the formation of a non-uniform bulk fluid.

For fluids with dilute impurities the asymptotic form of the structure factor derived here (see Eq. (18)) is expected to be a useful generalization of the standard Ornstein-Zernike form, because additional information on the impurity-solvent interactions can be extracted (see Eq. (20)). Application in future experimental studies on such systems would be highly welcome in order to test the derived expression further. Finally, the Ornstein-Zernike approach can be applied to multicomponent impurities, i.e., $i \in \{1, 2, 3, \dots, N\}$.

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